

AN EPOXY-BASED ELECTRICALLY INSULATING ADHESIVE
FOR THE PREVENTION OF ELECTROLYTIC CORROSION

5 The present invention relates to an epoxy-based electrically insulating adhesive for the prevention of electrolytic corrosion, of particular use in the electric/electronic industry.

10 For electrically insulating adhesives in the electric/electronic industry, two-component type epoxy-based adhesives are so far known. Particularly, from the aspect of electric characteristics, two-component
15 type epoxy adhesives with an acid anhydride as a curing agent are known. And, for the curing agent used in the two-component type epoxy adhesives which will harden at room temperature, aliphatic amines, aromatic amines, alicyclic amines, mercaptans, etc. are generally known.

20 However, conventional room temperature setting epoxy adhesives known in the electric/electronic industry are practically insufficient in their ability to maintain electric insulation, and besides they have the property to generate electrolytic corrosion under a condition wherein
25 moisture is given and voltage is applied. Because of this, for the purpose of room temperature setting adhesion for use in the electric/electronic industry wherein there are regions to be electrically insulated, adhesives having practically sufficient performances are not yet available.
30 When an acid anhydride is used as a curing agent, epoxy adhesives do not harden at room temperature, and high temperature for a long period of time is required to harden them.

British Patent Specification No. 950928 discloses a cold curable resin composition for use as a facing or surfacing material, which composition comprises:

- 5 1. a polyepoxide, preferably the combination of a glycidyl polyether and a polyhydric phenol;
2. an alkyl substituted monohydric phenol, and
3. a bituminous material.

The polyepoxide preferably comprises at least 10% by weight of the total mixture, more preferably 10 to 70%,
10 the alkyl substituted phenol from 3 to 85% and the bituminous material from 30 to 65% by weight of the total mixture. The compositions when combined with a hardening agent, such as a cycloaliphatic amino compound are said to cure to form a hard, durable homogeneous coating. The
15 cycloaliphatic amino compounds are used in an amount from 3 to 15% by weight of the polyepoxide. The use of such resin compositions is confined in the main to the surfacing of roads, pavements etc.

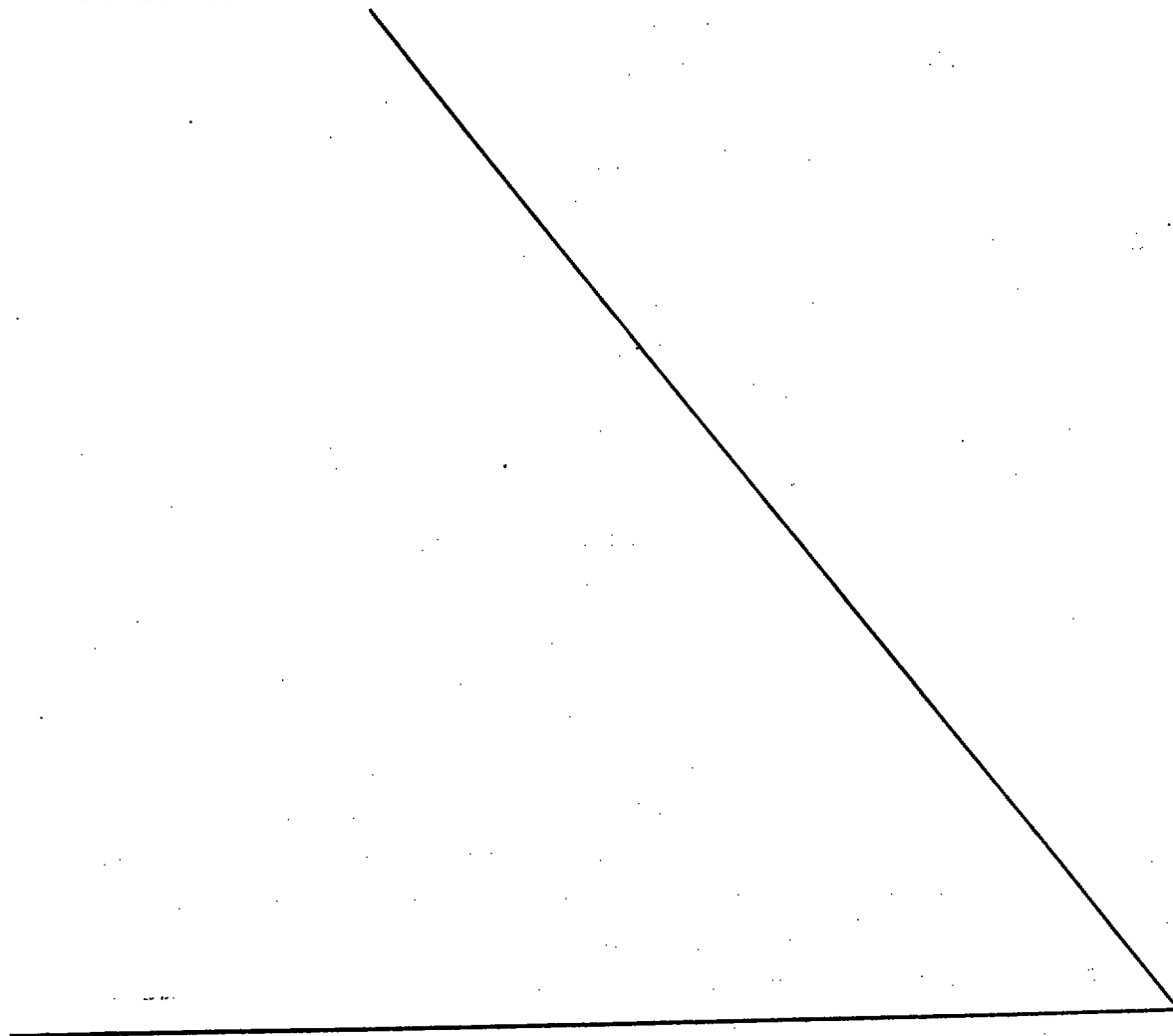
U.S. Patent No. 3,629,181 discloses adducts suitable for use as curing agents for epoxide resins, comprising:

- 20 1. a polyglycidyl ether of a polyphenol, which is liquid at room temperature, and,
2. a cycloaliphatic or cycloaliphatic-aliphatic di-primary diamine in which at least one of the primary amino
25 groups is bonded to an endocyclic carbon atom of the cycloaliphatic ring.

The composition comprises from 1.5 to 2.7 moles of the diamino (2) per 1 epoxide equivalent. The adducts are mixed with a liquid epoxide resin to provide a ready-to-
30 use composition suitable for the formation of lacquers, coating materials, adhesives and impregnating, dipping and casting resins. The compositions are said to be capable of curing at room temperature and in order to promote curing, cure promoting agents, such as phenols may be
35 added to the composition. The curing agent comprises up to 18% by weight of the total weight of the ready-to-use

composition. The adduct compositions of U.S. Patent No. 3,629,181 comprising diamine, polyepoxide and phenol, e.g., as shown in Example 1 of Manufacture, do not cure at room temperature, but rather form a storage-stable liquid solution which must subsequently be added to a second epoxide solution to give a ready-to-use lacquer.

U.S. Patent Specification No. 4,296,004 discloses polycyclic amino compounds of specified formula as epoxy resin curing agents and the use of nonylphenol to achieve more rapid curing of the resin. There is no indication of the intended use, or of properties such as cure temperature, electrical conductivity, corrosion resistance etc.



According to the present invention there is provided a room temperature curable electrically insulating adhesive comprising (a) a polyfunctional epoxy compound having two or more epoxy groups per molecule, (b) at least one alicyclic amine in an amount from 15 to 40 parts by weight per 100 parts of said epoxy compound, and (c) phenol or an alkylphenol in an amount from 10 to 60 parts by weight per 100 parts of said epoxy compound.

The adhesive has an insulation resistance of at least about $1 \times 10^{10} \Omega$ and an initial volume resistivity of at least about $1 \times 10^{13} \Omega \text{ cm}$, generates no electrolytic corrosion, and hardens at room temperature.

The polyfunctional epoxy compound may comprise any general purpose epoxy compound or epoxy resin having two or more epoxy groups per molecule. Examples of such polyfunctional epoxy compounds having two or more epoxy groups per molecule include Epon 828 (produced by Shell Co., Ltd.), YDF-170 (produced by Toto Kasei Co., Ltd.), ESCN-220 (produced by Sumitomo Chemical Co., Ltd.), Epiclon 152 (produced by Dainippon Ink & Chemicals Inc.), ED-503 (produced by Asahi Electro-Chemical Co., Ltd.), MK-107 (produced by Wilmington Chemical Co., Ltd.) and DER-736 (produced by Dow Chemical Co., Ltd.). The epoxy compound or resin preferably has an epoxy equivalent of from 180 to 195.

The alicyclic amine is used as a curing agent, and examples of those which can preferably be used include 4,4'-diaminodicyclohexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 1,3-bis(aminomethyl)-cyclohexane, 2-amino-2-(4-amino-4-methylcyclohexyl)propane and 3-aminomethyl-3,5,5-trimethylcyclohexylamine.

Phenol or an alkylphenol is used as a cure accelerator. An alkylphenol means a phenol derivative in which the benzene nucleus has been substituted with from 1 to 5 alkyl groups, and examples include cresol, trimethylphenol, xylenol, p-tert-butylphenol, p-octylphenol, nonylphenol, laurylphenol and stearylphenol.

As to the blending ratio of the composition of the present invention, the following amount of each

component are used, based on 100 parts by weight of the epoxy compound or epoxy resin, keeping in mind the practical aspects such as the curing rate, electrical insulation characteristics and electrolytic corrosion prevention characteristics of the adhesive. The amount of the alicyclic amine is a stoichiometric amount based on the epoxy compound or epoxy resin and comprises from 15 to 40 parts by weight per 100 parts of said epoxy compound; and the amount of phenol or alkylphenol from 10 to 60 parts by weight per 100 parts of said epoxy compound.

Specifically, a particularly preferred amount of the alicyclic amine is from 25 to 35 parts by weight for 4,4'-diaminodicyclo-hexylmethane; from 30 to 40 parts by weight for 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane; from 21 to 29 parts by weight for 1,3-bis(aminomethyl)-cyclohexane; from 19 to 29 parts by weight for 2-amino-2-(4-amino-4-methylcyclohexyl)propane; and from 20 to 28 parts by weight for 3-aminomethyl-3,5,5-trimethylcyclohexylamine. The amount of the cure accelerator is preferably from 10 to 20 parts by weight for phenol; and from 40 to 60 parts by weight for an alkylphenol.

When the amount of the alicyclic amine is less than 15 and particularly less than about 10 parts by weight, the stiffness of cured products decreases, and when it exceeds 40 and particularly above about 50 parts by weight, the amount of the amine which remains unreacted increases to bring about a reduction in electrical insulation ability and electrolytic corrosion resistance.

When the amount of phenol is less than 10 and particularly less than about 5 parts by weight, the curing rate slows down, and when it exceeds 60 and particularly above about 70 parts by weight, the stiffness of cured products decreases.

The adhesive of the present invention may contain other components such as plasticizers, solvents, etc., which are conventionally contained in the common adhesives, in the usual proportions.

5 The present invention will be illustrated in more detail with reference to the following examples, but it is not limited to these examples. In the examples, all parts are by weight.

10 Volume resistivity described in the examples and comparative examples was measured by the method of JIS K 6911, and insulation resistance and generation of electrolytic corrosion under a condition wherein moisture is given and voltage is applied were measured by the following test methods:

15 (1) The adhesive is coated at a thickness of 1 mm onto a portion enclosed within a test body (comb-form electrode).

20 (The comb-form electrode is made of a solder resist-free glass epoxy board (grade, FR-4), its circuit width being 0.8 mm and the space between circuits being 0.8 mm.)

(2) The adhesive is hardened at 25°C for 7 days.

25 (3) The test body is exposed to an atmosphere of 60°C and 95% RH for 1000 hours while causing a DC of 100 V to flow between the electrodes.

(4) Generation of electrolytic corrosion is macroscopically observed and judged.

(5) After charging 500 V for 1 minute between the electrodes, insulation resistance is measured at 25°C.

30 Adhesion shear strength described in the examples and comparative examples was measured by the following test method:

35 (1) The adherend is a glass epoxy board of 2.0 mm x 25 mm x 100 mm (length) and it is used after defatting with a solvent.

(2) The adhesive is coated onto a portion of 25 mm x 12.5 mm (length) on the surface of the adherend, and adhered to another glass epoxy board of the same size; after fixing the both boards with a binder clip, the
5 adhesive is hardened.

(3) Measurement is made on a tensile tester at a tension rate of 5 mm/min.

Examples 1 to 9 and Comparative Examples 1 to 4

10 Preparation of adhesives used in Examples 1 to 9. and
Comparative Examples 1 and 2.

An alicyclic amine and phenol or alkylphenol were added to a 225 ml glass container in compositions and amounts described in Table 2, and stirred at 60°C for 1
15 hour by means of a magnetic stirrer to obtain a uniform mixture. To this mixture was added a polyfunctional epoxy compound, and the resulting mixture was rapidly stirred at room temperature by means of a mixer having a stirring blade of 20 mm in diameter to obtain a uniform adhesive.

20 Preparation of adhesives used in Comparative Examples 1 and 2

The protocol used to prepare the adhesive compositions of Examples 1 to 9 was repeated using 4,4'-diaminodiphenylmethane/Epon 828 adduct (Comparative
25 Example 1) and polyethylene glycoldiamine (Comparative Example 2) as the amine compound.

Preparation of adhesives used in Comparative Example 3

Polyoxpropylene-2-hydroxy-3-thiolpropane alkyl ether and 2,4,6-tris(dimethylaminomethyl)phenol were added to a
30 225 ml glass container in an amount described in Table 1, and stirred at room temperature for 15 minutes by means of a mixer having a stirring blade of 20 mm in diameter to obtain a uniform mixture. To this mixture was added the polyfunctional epoxy compound, and the resulting mixture
35 was rapidly stirred at room temperature by means of the same mixer to obtain a uniform adhesive.

Characteristics

5 The adhesives prepared as described above were each coated onto a glass epoxy board, and the various characteristics were measured (Examples 1 to 9 and Comparative Examples 1 to 3). Similarly, the same characteristics on a glass epoxy board coated with no adhesive were measured (Comparative Example 4). The results are shown in the following tables.

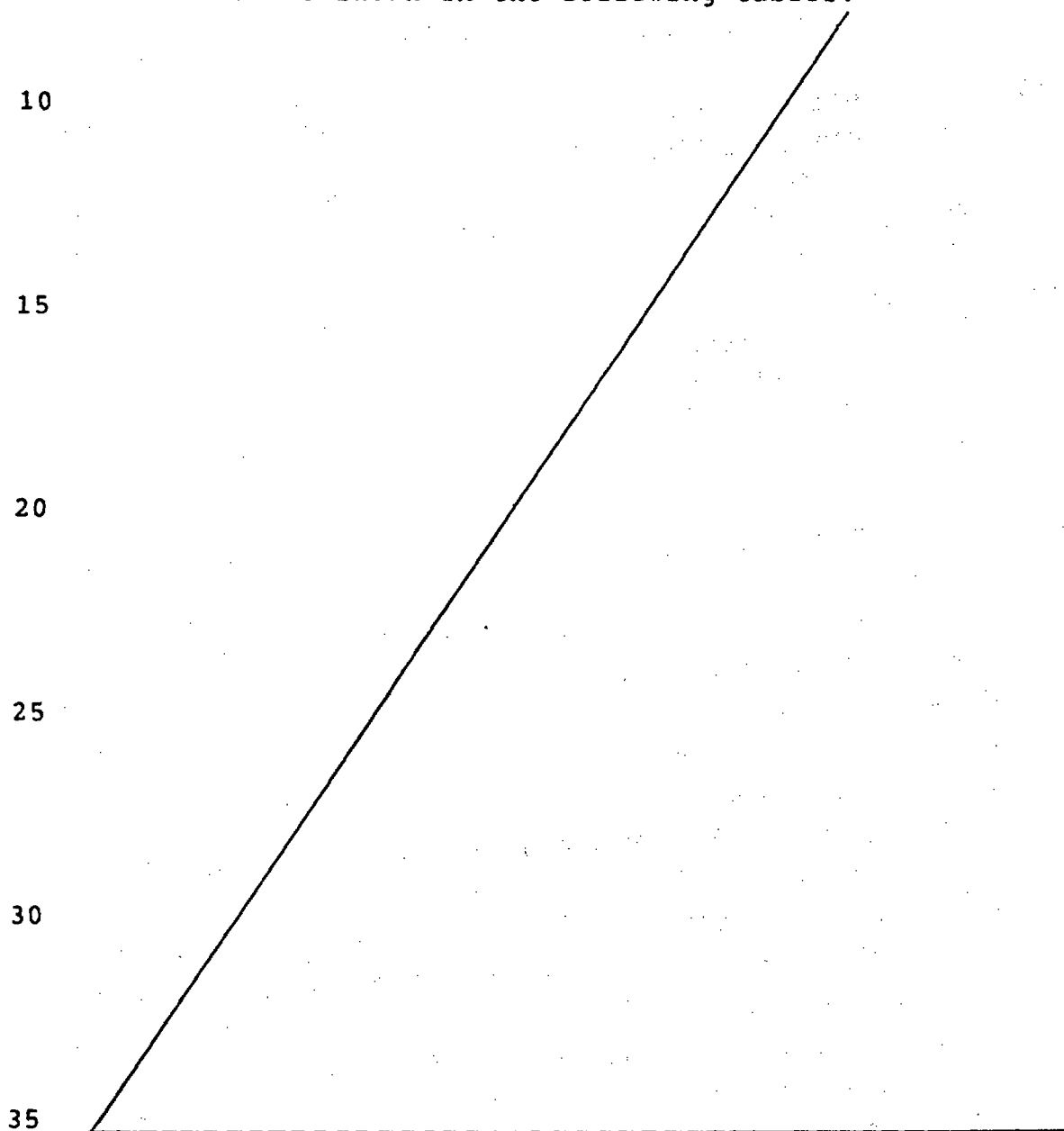


Table 1 Table of Composition and Performance of Adhesive

Composition, Amount (Part) and Performance	Comparative Example			
	1	2	3	4
5 Epon 828 4,4'-Diaminodicyclohexylmethane 3,3'-Dimethyl-4,4'-diaminodicyclohexylmethane 1,3-Bis(aminomethyl)cyclohexane 2-Amino-2-(4-amino-4-methylcyclohexyl)propane 3-Aminomethyl-3,5,5-trimethylcyclohexylamine 4,4'-Diaminodiphenylmethane/Epon 828 adduct Polyethylene glycoldiamine Polyoxypropylene-2-hydroxy-3-thiolpropane alkyl ether	100	100	100	
10	60			
15 Phenol Cresol Nonylphenol 2,4,6-Tris(dimethylaminomethyl)phenol Volume resistivity (Ω cm) Insulation resistance (Ω) Initial stage 60°C/95% RH, 1000 hrs Generation of electrolytic corrosion Adhesion shear strength (kg/cm ²)	10 10 10 3.2x10 ¹⁵ 3.5x10 ¹² 8.5x10 ¹⁰ Observed 150	10 10 10 2.5x10 ¹³ 8.5x10 ¹² 3.0x10 ¹⁰ Observed 200	10 8.9x10 ¹³ 3.5x10 ¹³ 3.2x10 ⁸ Observed 50	 3.5x10 ¹³ 2.0x10 ¹⁰ Observed

Note: The number of days (at room temperature) required for the adhesive to harden until it shows the same performances as shown in the Table is about 2 for Examples 1 to 9.

Table 2 Table of Composition and Performance of Adhesive

Composition, Amount (part) & Performance		Example								
1	2	3	4	5	6	7	8	9		
5 Epon 828	100	100	100	100	100	100	100	100		
4,4'-Diaminodicyclo- hexylmethane	30									
3,3'-Dimethyl-4,4'- diaminodicyclo- hexylmethane		35								
1,3-Bis(aminomethyl)- cyclohexane			25							
2-Amino-2-(4-amino- 4-methylcyclo- hexyl)propane										
3-Aminomethyl-3,5,5- trimethylcyclo- hexylamine			22							
4,4'-Diaminodiphenyl- methane/Epon 828 adduct									24	
Polyethylene glycoldiamine										
Polyoxypropylene-2- hydroxy-3-thiol- propane alkyl ether										

Table 2 Table of Composition and Performance of Adhesive (Continued)

Composition, Amount (part) & Performance	Example								
	1	2	3	4	5	6	7	8	9
5 Phenol	10	10	10	10	10	10	10		
Cresol								40	
Nonylphenol									60
2,4,6-Tris(dimethyl- aminomethyl)phenol									
10 Volume resistivity (Ω cm)	3.2x10 ¹⁵	2.0x10 ¹⁵	2.5x10 ¹⁵	4.3x10 ¹⁵	3.3x10 ¹⁵	3.5x10 ¹⁵	3.0x10 ¹⁵	3.3x10 ¹⁵	4.2x10 ¹⁵
Insulation resistance Initial stage	3.4x10 ¹³	3.2x10 ¹³	2.8x10 ¹³	3.4x10 ¹³	2.5x10 ¹³	3.0x10 ¹³	2.5x10 ¹³	3.3x10 ¹³	3.5x10 ¹³
60°C/95% RH, 1000 hrs Generation of electrolytic corrosion	2.5x10 ¹¹	3.5x10 ¹¹	1.8x10 ¹¹	2.8x10 ¹¹	8.8x10 ¹⁰	1.7x10 ¹¹	1.5x10 ¹¹	1.8x10 ¹¹	2.2x10 ¹¹
	Not Observed	Not Observed	Not Observed	Not Observed	Not Observed	Not Observed	Not Observed	Not Observed	Not Observed
20 Adhesion shear strength (kg/cm ²)	220	200	230	210	210	200	200	240	200

As illustrated above, by applying the adhesive of the present invention at room temperature, it has become possible to obtain excellent volume resistivity and maintain a high insulation resistance even under a
5 condition wherein moisture is provided and voltage is applied for a long period of time. Also, it has become possible to completely prevent the generation of electrolytic corrosion. Further, the adhesive of the present invention satisfactorily hardens even at room
10 temperature, so that the operation condition has become markedly lightened. Thus, it has become possible by the present invention to provide an adhesive which can satisfactorily be put to practical use at room temperature not only in the fixation/adhesion of parts in the
15 electric/electronic area requiring electric insulation reliability, but also in potting and casting.

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The drawing shows a test pattern used in the test
20 for electric insulation/electrolytic corrosion characteristics.

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CLAIMS

1. A room temperature curable electrically insulating adhesive comprising (a) a polyfunctional epoxy compound having two or more epoxy groups per molecule, (b) at least
5 one alicyclic amine in an amount from 15 to 40 parts by weight per 100 parts of said epoxy compound, and (c) phenol or an alkylphenol in an amount from 10 to 60 parts by weight per 100 parts of said epoxy compound.
 2. An adhesive as claimed in Claim 1 in which alicyclic
10 amine is selected from 4,4'-diaminodicyclohexylmethane, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane, 1,3-bis(aminomethyl)cyclohexane, 2-amino-2-(4-amino-4-methylcyclohexyl)propane and 3-aminomethyl-3,5,5-trimethylcyclohexylamine.
 - 15 3. An adhesive as claimed in Claim 1 or Claim 2 in which the alkylphenol is selected from cresol, trimethylphenol, xlenol, p-tert-butylphenol, p-octylphenol, nonylphenol, laurylphenol and stearylphenol.
 4. An adhesive as claimed in Claim 1 substantially as
20 herein described with reference to any one of the Examples.
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